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A paper presented on May 21, 1969, at the Eighty-Ninth Annual Conference, American Water Works Association, San Diego, California, by Percy P. St. Amant, Director, San Joaquin Project, Federal Water Pollution Control Administration, U. S. Department of the Interior, P. O. Box 2385, Fresno, California, and Perry L. McCarty, Professor of Environmental Engineering, Stanford University, Stanford, California.

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Percy P. St. Amant and Perry L. McCarty*

The U. S. Public Health Service Drinking Water Standards of 1962 (1) recommend that nitrates in drinking water be limited to 45 milligrams per liter. This is equivalent to 10 milligrams per liter of nitrate-nitrogen. This limit has been set because of the association of high nitrates in water with the incidents of methemoglobinemia in infants. At the time when the standards were put into effect, the lack of an economical method for the removal of excess nitrates was acknowledged. Thus, seeking other water supplies or warning the population in the high nitrate areas of the potential danger of using the water for infant feeding and informing them of alternate sources was suggested.

The results of recent investigations on the removal of nitrates from irrigation return waters in the San Joaquin Valley in California have indicated that biological denitrification may be an economically feasible way to remove nitrates. These investigations have been conducted by an interagency group composed of the California Department of Water Resources, the Federal Water Pollution Control Administration, and the Bureau of Reclamation (2). The primary purpose has been to develop methods to control the discharge of undesirable

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quantities of nitrates into the San Francisco Bay System rather than to develop a process for nitrate removal from a municipal water supply. However, of the several processes studied, biological denitrification in filter beds has proved to have the stability and efficiency of operation that would be necessary for treatment of a drinking water supply. This paper contains a summary of the pilot-plant studies which were conducted to estimate chemical requirements, to evaluate possible filter media, and to determine the important operating parameters.

Biological Denitrification

During biological denitrification, nitrates and nitrites are reduced to nitrogen gas, a harmless material which makes up 78 percent of the earth's atmosphere. The ability to bring about denitrification is characteristic of a wide variety of common facultative bacteria including the genera Pseudomonas, Achromobacter, and Bacillus. Denitrification can be carried out only if the organisms are supplied with an organic energy source (or an inorganic energy source for certain autotrophic bacteria), and only if oxygen is not available. Under such anaerobic conditions, the microorganisms can use nitrates or nitrites as terminal electron acceptors to bring about the oxidation of the energy source, just as oxygen is used under aerobic conditions.

Since drinking water supplies are essentially free of organic material, it would be necessary to add some to achieve denitrification. The most inexpensive organic materials which appeared suitable for denitrification were sugar, acetic acid, ethanol, acetone, and methanol. Preliminary studies indicated all would give satisfactory results but

methanol was the least expensive (3). Also, the cost for methanol is expected to drop in the future because of the development of new technology for its production. Although methanol is a known poison, it is felt safe for use at the low concentrations required.

The quantity of methanol which is needed for denitrification can be estimated from its reaction with nitrates and from a consideration of the quantity required for bacterial synthesis. Denitrification of nitrates is a two-step process:

First Step:

$$NO_3^- + 1/3\ CH_3OH \rightarrow NO_2^- + 1/3\ CO_2 + 2/3\ H_2O \quad (1)$$

Second Step:

$$NO_2^- + 1/2\ CH_3OH \rightarrow 1/2\ N_2 + 1/2\ CO_2 + 1/2\ H_2O + OH^- \quad (2)$$

Overall:

$$NO_3^- + 5/6\ CH_3OH \rightarrow 1/2\ N_2 + 5/6\ CO_2 + 7/6\ H_2O + OH^- \quad (3)$$

Thus, one mole of nitrate requires at least 5/6 moles of methanol for complete denitrification, or 1.90 milligrams per liter of methanol is required for each milligram per liter of nitrate-nitrogen. If less methanol is added, the reaction will not go to completion. The result would be a water high in nitrites. This is undesirable as such a water would have a high chlorine demand, making the cost of the overall process greater than the cost of the methanol saved.

If the water contains dissolved oxygen, then this must be removed before denitrification will occur. This can be accomplished biologically by the addition of more methanol:

$$O_2 + 2/3\ CH_3OH \rightarrow 2/3\ CO_2 + 4/3\ H_2O \quad (4)$$

Each milligram per liter of dissolved oxygen would require at least 0.67 milligrams per liter of methanol for its removal.

Methanol must also be supplied to satisfy the requirements for bacterial growth. The amount for this purpose can be evaluated from the consumptive ratio which is defined as the ratio of the total quantity of chemical required for denitrification to the stoichiometric requirement for denitrification and deoxygenation alone. The consumptive ratio for methanol has been evaluated to be 1.30 (3). This means an additional 30 percent of methanol must be added over the stoichiometric amounts given by Equations 2, 3, and 4 in order to satisfy the bacterial growth requirements. From these considerations a formula can be developed to evaluate the total concentration of methanol required for complete denitrification.

$$C_m = 2.47\ N_o + 1.53\ N_1 + 0.87\ D_o \qquad (5)$$

where:

C_m = required methanol concentration, mg/l

N_o = initial nitrate-nitrogen concentration, mg/l

N_1 = initial nitrite-nitrogen concentration, mg/l

D_o = initial dissolved oxygen concentration, mg/l

For most natural waters, N_1 is zero.

Field Studies

As mentioned, one method of nitrate removal under active evaluation at the Interagency Agricultural Waste Water Treatment Center near Firebaugh, California, is filter denitrification. A schematic diagram of this process is shown in Figure 1. An organic

material (methanol) is added to the agricultural wastewater just before it enters the bottom of the filter and flows upward. The characteristics of the agricultural wastewaters used in field evaluation of the filters are listed in Table 1. This water is obtained from subsurface drains and is characteristic of a highly saline ground water.

A number of pilot-plant denitrification filters have been operating under field conditions for approximately one year. Both 18-inch and 36-inch diameter filters are under evaluation. All filters have a bed depth or media depth of six feet.

The major variables investigated have been filter media and detention time. Some of the various media investigated include sand, activated carbon, volcanic cinders, gravel, coal, and a commercially produced plastic trickling filter media. Various media sizes from coarse sand to 3-inch diameter gravels have been used. The detention times studied ranged from one-half hour to two hours, representing flow rates from approximately 0.6 gallons per minute per square foot to 0.15 gallons per minute per square foot.

The organic carbon (methanol) requirements for denitrification of the agricultural wastewater has been close to the estimated quantity given by Equation 5. In order to achieve more than 90 percent reduction of the 20 mg/l of influent nitrate-nitrogen, approximately 60 mg/l of methanol is required.

As would be expected in a biological system, the efficiency of the denitrification filter is affected by the temperature of the

wastewater. The greatest drop in efficiency occurred when the temperature of the wastewater was below approximately 10°C. A filter is presently being operated within a controlled environment so the effect of temperature can be carefully monitored and studied.

The filters with sand were very efficient initially, but after several months of operation they experienced some clogging due to a dense microorganism buildup at the bottom of the filters. This clogging caused excessive head loss through the filter. Similar problems occurred with activated carbon.

Of the media evaluated, the most satisfactory has been the one-inch diameter gravel. A filter with this media has been in operation for approximately nine months at a detention time of one hour. The average total nitrogen removal for this period has been approximately 90 percent of the 20 mg/l of influent nitrate-nitrogen. This efficiency has been maintained even though the influent water reached a low temperature of 12°C. At this temperature, however, the efficiency of a similar filter operating at a one-half hour detention time dropped to about 70 percent. During the total period of operation, it has not been necessary to clean the filter and the head loss is presently only about 4.3 psig. Results of operation of this filter are listed in Table 2.

Characteristics of Denitrified Water

Water which has undergone denitrification is not dark and odorous, as might be suggested from familiarity with some anaerobic waters. Denitrification is not an anaerobic reaction in the usual

sense. It is similar to aerobic oxidations with nitrates rather than oxygen used as the electron acceptor. Under such conditions, the production of reduced and odorous organic and inorganic end products such as indol, skatol, or hydrogen sulfide does not occur. However, these end products could form if more organic material than required for denitrification were added. For this reason the organic dosage must be carefully controlled.

There are some constituents in denitrified water which must be given further consideration. The treated water will contain some nitrate, nitrite, and ammonia nitrogen. It may contain some residual methanol, it will have some turbidity resulting from biological solids that are carried out of the filter, and it will be devoid of dissolved oxygen. The Public Health Service Drinking Water Standards have no limit on nitrite-nitrogen, but this is probably less desirable in drinking water than nitrates. It is the nitrites formed by the reduction of nitrates in infants' stomachs which is directly implicated in methemoglobinemia. However, chlorination of the treated effluent should result in the oxidation of nitrite to nitrate:

$$NO_2^- + Cl_2 + H_2O \rightarrow NO_3^- + 2\ H^+ + 2\ Cl^- \qquad (6)$$

Each milligram per liter of nitrite-nitrogen will exert a chlorine demand of 5.06 milligrams per liter, which will add to the cost of treatment. In addition, the ammonia nitrogen that is formed will react to form chloramines, which may or may not be detrimental.

The residual methanol is probably too low in concentration to be of public health significance. A fatal dose of methanol is

about 100 to 250 milliliters, although death from less than 30 milliliters has been reported (4). Daily consumption of the milligram per liter quantities of methanol in a denitrified water would be 4 to 5 orders of magnitude less than a toxic concentration. From another viewpoint, the maximum allowable concentration for methanol in air, based on industrial hygiene standards, is 200 parts per million (5). Air with such a methanol concentration would equilibrate with water to form an aqueous concentration of several hundred milligrams per liter. Thus the equilibrium partial pressure of a few milligrams per liter of methanol in water is far below the equivalent industrial standards.

Perhaps the major detrimental effect of the excess methanol is its oxygen-consuming potential. Aeration of the treated water would appear desirable both for this reason and to remove the slight musty odor associated with the water when devoid of oxygen. This requires further exploration.

The quantity of methanol converted to biological solids has already been discussed. The weight of excess microorganisms produced would be about equivalent to this quantity. For example, if a raw water contained 40 milligrams per liter of nitrate-nitrogen and 8 milligrams per liter of dissolved oxygen, the microorganism production from denitrification would be about 23 milligrams per liter (3). Much of the biological mass would remain in the filter, but eventually would either need to be removed or would escape in the effluent. The effluent biological solids are, in general,

well flocculated, so they should need no chemical coagulation for removal. Filtration of some type would be necessary. Other physical characteristics of the denitrified water, such as taste and odor potential, still need to be evaluated.

Process Design and Cost

A suggested flow plan of a water treatment plant for nitrate removal is illustrated in Figure 2. There is no need to reduce the nitrate-nitrogen level below the Drinking Water Standards suggested value of 10 milligrams per liter. However, sufficient organic material must be added to achieve complete reduction of nitrates to nitrogen gas in the portion denitrified, in order to prevent a partial reduction to nitrites only. The desired 10 milligrams per liter of nitrates in the effluent is then achieved by mixing the denitrified water with some of the raw water. High nitrate waters are invariably from well supplies so that, in general, no filtration of the by-passed water would be necessary.

Aeration might be achieved by allowing the denitrified water to flow over splash pans as are commonly used for iron removal. There are other possibilities. Filtration would be necessary, but a high rate process could perhaps be used because of a low concentration of well flocculated biological solids which would have to be removed. Chlorination of the blended mixture should be used to insure oxidation of any residual nitrites as well as to achieve disinfection.

Based on the results of the field investigation, rounded

stone, 1 to 2 inches in diameter, is recommended for the denitrification media. A theoretical detention time of about one hour is required to insure complete denitrification provided the water temperature is 12°C or higher. At lower temperatures a longer detention time would be necessary, and if the temperatures were too close to the freezing point the process may fail.

The best design for a large-scale denitrification filter can only be speculated upon at this time since sufficient experience with such a unit is not yet available. A 10-foot square filter, six feet in height, has been built at the field site near Firebaugh, California, to evaluate hydraulic characteristics. This filter has a false bottom as used for rapid sand filter construction for water treatment. The water will enter through this bottom, will rise through the stone media, and will be collected at the top with a system of wiers. No special provision for the removal of excess biological solids accumulation in the filter has been provided. The experience with smaller diameter filters has indicated that they can be operated for many months without this becoming a problem. When excessive head loss does occur, removal of the biological solids will be attempted by increasing the hydraulic flow rate through the filter for a short period.

The estimated cost of the denitrification process alone per 1,000 gallons of water delivered to the customer is listed in Table 3. Costs for aeration, filtration, and chlorination after denitrification are not included. The percent water requiring

denitrification was based on an estimated 90 percent removal of nitrate plus nitrite by the denitrification process and the production of a combined water meeting the Drinking Water Standards of 10 milligrams per liter of nitrate-nitrogen. Capital costs were based on an estimated $2.00 per cubic foot for the stone media in place, an interest rate of 4 percent, and a design period of 20 years. Chemical costs were estimated using Equation 5 and a current cost (1969) for methanol of 25¢ per gallon (6.63 pounds). These estimates are quite tentative and should be viewed with caution. However, they do indicate that the cost for denitrification is in line with costs for chemical treatment of a turbid water supply. The cost rises with increase in nitrate-nitrogen but not in a linear fashion, since a higher portion of the water must be treated at a higher nitrate concentration.

Conclusions

1. Biological denitrification in anaerobic filters is a reliable process for removing excess nitrates from water supplies.
2. An organic electron donor must be added to accomplish denitrification and methanol has been found to be a satisfactory and inexpensive material for this purpose.
3. Use of one-inch gravel filter media and a detention time of one hour is sufficient for 90 percent or greater removal of approximately 20 mg/l of nitrate-nitrogen in water with temperature of 12°C and above.

4. Careful control of the feeding of methanol is required to prevent problems resulting either from underdosage or overdosage.
5. Additional research is required to determine the hydraulic characteristics of large-scale filters and to evaluate the palatability of the denitrified water.

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TABLE 1

CHARACTERISTICS OF WATER USED ON FIELD
EVALUATION OF FILTER DENITRIFICATION

Constituent	Range of Concentration mg/l
Total Dissolved Solids	2500 - 7600
Suspended Solids	0 - 5
Alkalinity (as $CaCO_3$)	280 - 330
Chloride	310 - 640
Sulfate	1500 - 3900
Nitrogen	
Nitrate-N	15 - 26
Nitrite-N	0
Ammonia-N	0
Organic-N	0.1 - 0.7
Total-N	15.1 - 26.7
C.O.D.	10 - 20
Dissolved Oxygen	7 - 9
pH	7.5 - 8.3

TABLE 2

CHARACTERISTICS OF OPERATION OF ANAEROBIC FILTER WITH ONE-INCH GRAVEL MEDIA AND ONE-HOUR DETENTION TIME

Day of Operation	Water Temp. °C		Nitrogen Concentration - mg/l								Nitrogen Removal %
			Influent				Effluent				
	Min	Max	NO_3	NO_2	NH_3 + Org	Total	NO_3	NO_2	NH_3 + Org	Total	
2	Not Recorded		7.5	0.2	0.5	8.2	0.0	0.0	0.4	0.4	95
43	"	"	22.5	1.8	0.5	24.8	0.2	0.0	0.7	0.9	96
56	"	"	19.2	0.5	0.6	20.3	0.2	0.0	0.6	0.8	96
79	18	22	18.1	0.2	0.6	18.9	0.0	0.0	1.0	1.0	95
89	18	20	19.1	0.0	0.5	19.6	0.0	0.1	0.9	1.0	95
103	16	19	17.1	0.0	0.4	17.5	0.0	0.1	0.5	0.6	97
112	17	19	16.5	0.0	0.4	16.9	0.0	0.1	0.6	0.7	96
145	13	14	18.4	0.0	0.4	18.8	0.5	0.4	0.6	1.5	92
165	13	16	18.4	0.0	0.5	18.9	0.9	0.8	0.5	2.2	88
239	13	14	15.0	0.0	0.2	15.2	0.1	0.3	0.8	1.2	92
241	12	14	17.9	0.0	0.2	18.1	0.1	0.5	0.8	1.4	92
248	12	14	15.4	0.1	0.7	16.2	0.2	0.4	0.8	1.4	91
255	12	16	18.3	0.0	0.5	18.8	0.2	0.8	0.9	1.9	90

TABLE 3

ESTIMATED FILTER SIZE, CHEMICAL REQUIREMENT, AND COST
FOR REMOVING NITRATE-NITROGEN FROM ONE MGD OF WATER

	Initial Nitrate-Nitrogen Concentration - mg/l	
	20	40
Initial Dissolved Oxygen Concentration	8 mg/l	8 mg/l
Portion of Water Requiring Treatment	55%	83%
Volume of Filter*	14,000 cu. ft.	21,000 cu. ft.
Filter Cost		
Total	$28,000	$42,000
Annual (20 year @ 4%)	$ 2,060	$ 3,090
Methanol Requirement		
Treated Water	57 mg/l	106 mg/l
Combined Water	31 mg/l	88 mg/l
Cost Per 1000 gallons of Combined Water		
Methanol	0.99¢	2.61¢
Filter Construction	0.56¢	0.84¢
Total	1.55¢	3.45¢

*Filter volume based on one-hour detention time, 50% excess capacity for maximum flows, and a void volume of 33%.

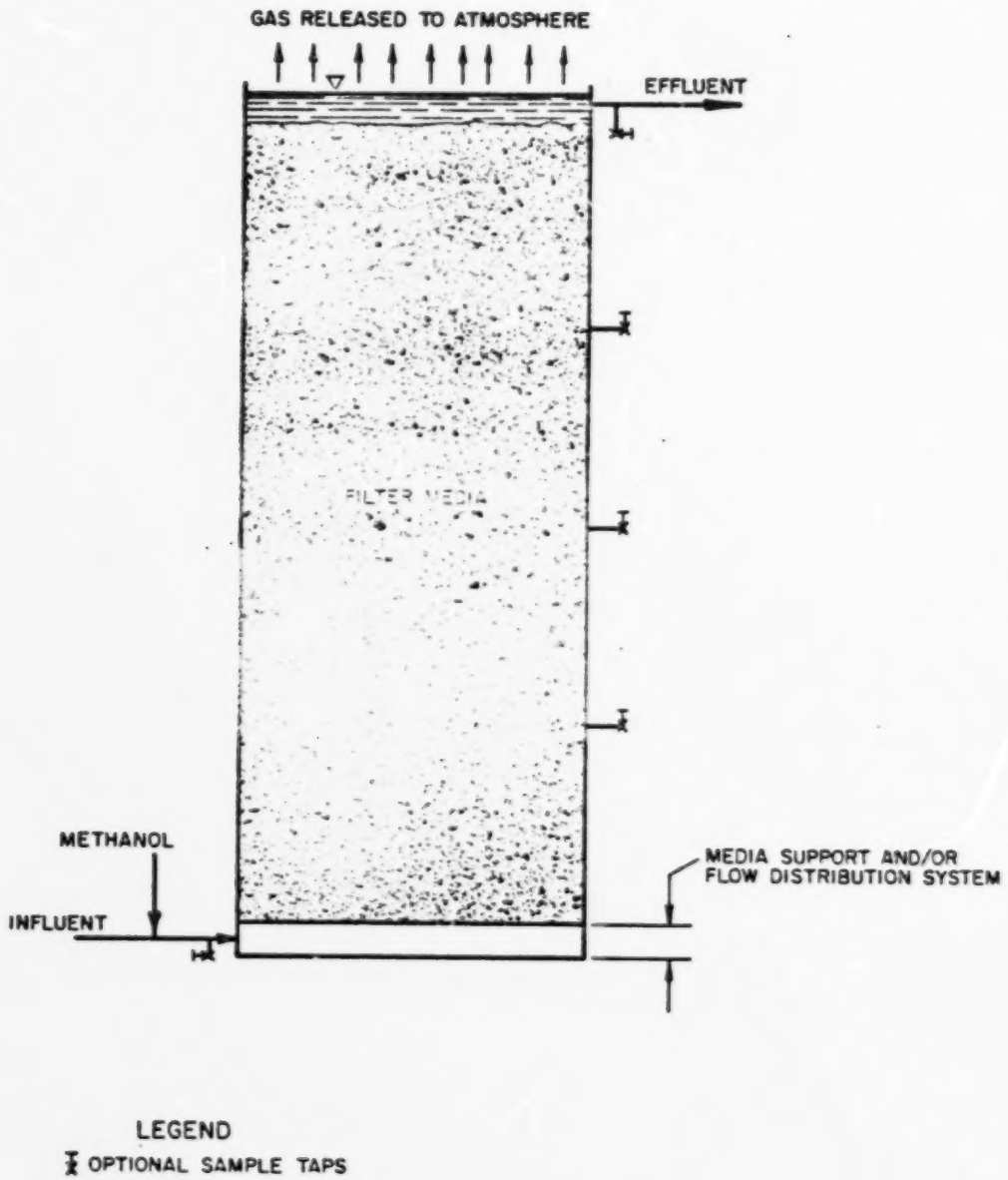

Figure 1. SCHEMATIC DIAGRAM OF DENITRIFICATION FILTER

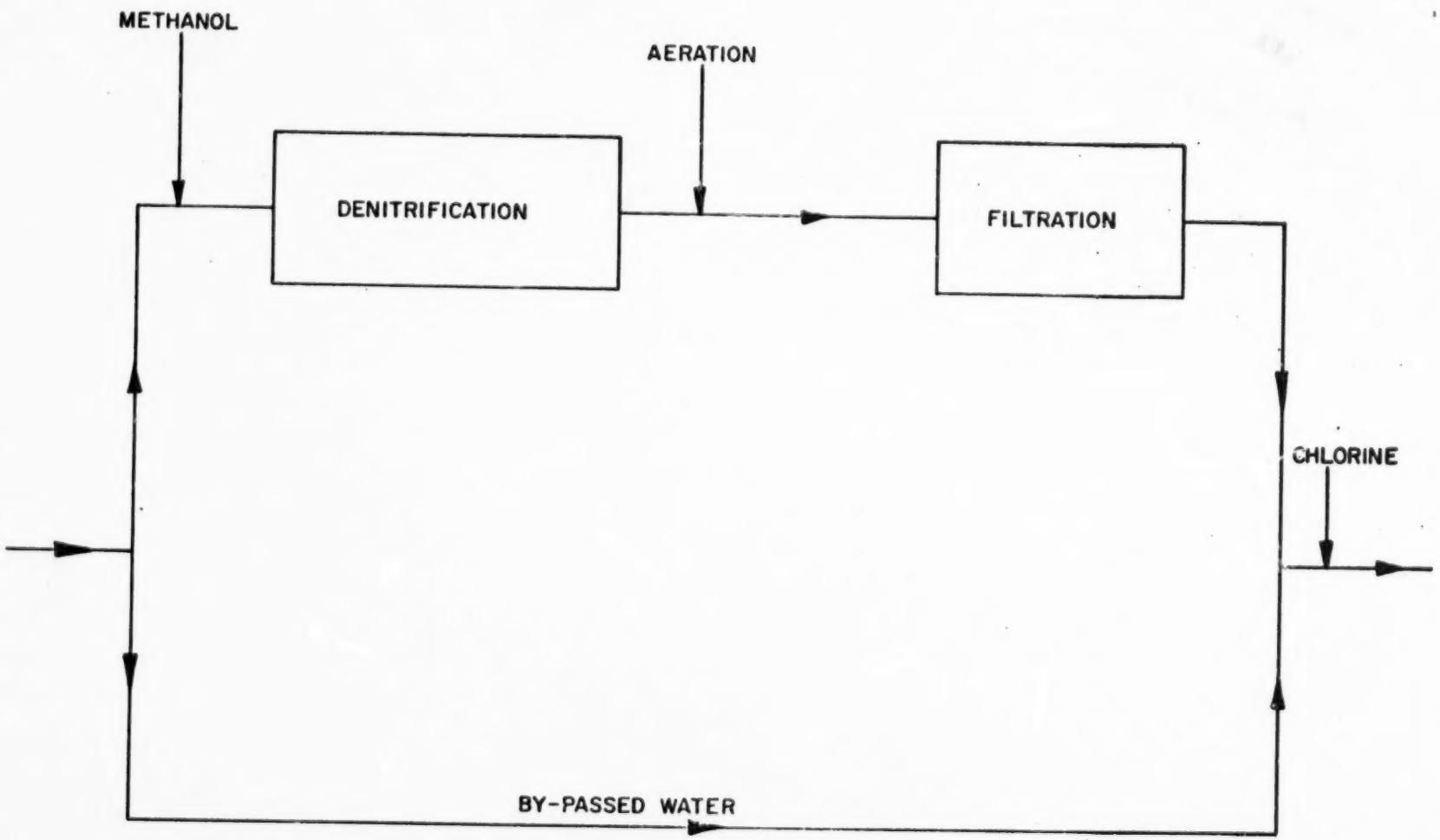

Figure 2. SCHEMATIC DIAGRAM FOR SUGGESTED DENITRIFICATION TREATMENT PLANT